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Investigation on the influence of nitrogen in process atmospheres on the corrosion behavior of brazed stainless steel joints

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Abstract. Brazing of stainless steels is commonly carried out using nickel-based brazing fillers, which provide a high corrosion and oxidation resistance of the resulting joints. These brazed stainless steel joints are mostly used for manufacturing of heat exchangers for energy and air conditioning technologies. The joints of the study were produced at temperatures of 1000 °C, 1125 °C and 1150 °C in vacuum furnaces or continuous furnaces. In both cases, the parts interact with process gases like nitrogen within the brazing process, especially during cooling. The amount of nitrogen in the braze metal as well as in the base material was determined by the carrier gas hot extraction technique. The occurring diffusion of nitrogen into the braze metal and the base material causes a shift in the corrosion potentials. In this work, the influence of the nitrogen enrichment on the corrosion behavior was investigated using a capillary microcell. The corrosion measurements were carried out on the braze metal and the base material. The results of samples, brazed with and without the influence of nitrogen, were compared.

1. Introduction

Brazed stainless steel components such as heat exchangers for energy and air conditioning technology are manufactured millions of times in a wide range of sizes and types. A significant part of these components is brazed with nickel-based fillers, which offer the highest corrosion and oxidation resistance of the resulting joints [1-3]. By alloying with the elements silicon, boron and phosphorus, the melting temperature of the nickel or the nickel-chromium matrix is reduced and thus brazing temperatures between 1000 °C to 1200 °C are possible. Nickel-based fillers like (NiCoCr)-B-Si amorphous brazing filler metals, Ni-Cr-Si-B-P amorphous brazing foils and new nickel-based brazing alloy Ni-29Cr-8Mo-xFe-ySi offer a great potential for joining of stainless steels. The processing, structure and properties of the resulting brazed joints have been extensively reported [4-6]. The alloying elements provide excellent flowing and wetting properties, because they are able to eliminate the oxide film on the surface of the base materials. However, the alloying elements adversely affect the microstructure and the mechanical properties of the joints when the gap size exceeds 50 µm [7]. The joints are commonly brazed in vacuum furnaces or continuous furnaces. Nitrogen (N₂) or mixtures of nitrogen and hydrogen (N₂+H₂) are commonly used as process gases in continuous furnaces. In vacuum furnaces, N₂ is often added during the cooling process. For this reason, a nitrogen enrichment takes place in the braze metal and in the near-surface area of the base material. However, the influence of the nitrogen enrichment on the properties of the brazed joints has not been investigated yet. In this context, it was supposed that nitrogen is able to influence the corrosion properties of stainless steel joints, brazed with nickel-based fillers [8]. In this



work, the influence of nitrogen in process atmospheres on the corrosion behavior of brazed stainless steel joints is investigated. The nitrogen content in the braze metal as well as in the base material is determined using the carrier gas hot extraction technique (CGHE). The influence of the nitrogen enrichment on the corrosion behavior is analyzed using a capillary microcell. The corrosion measurements are performed on the braze metal and the base material. The results of samples brazed with and without the influence of nitrogen are compared.

2. Experimental procedures

Austenitic stainless steel (AISI 304) was used as base material. The components to be brazed (circular and semi-circular blanks with a diameter of 30 mm) were made of finely rolled sheets by laser cutting, which leads to burr-free and distortion-free samples. The fillers Ni710, Ni60CrPSi and Ni650 were applied on the base material as powder. The thickness of the produced brazed joint was adjusted at 50 μm by means of inserted spacer foils, figure 1. The quantity of applied filler was the same for all samples and was dimensioned, such that a joint thickness of at least 50 μm was ensured on average. Binder for a brazing powder was avoided to eliminate carbon residues and their consequences, for example, the formation of chromium carbide in the braze metal.

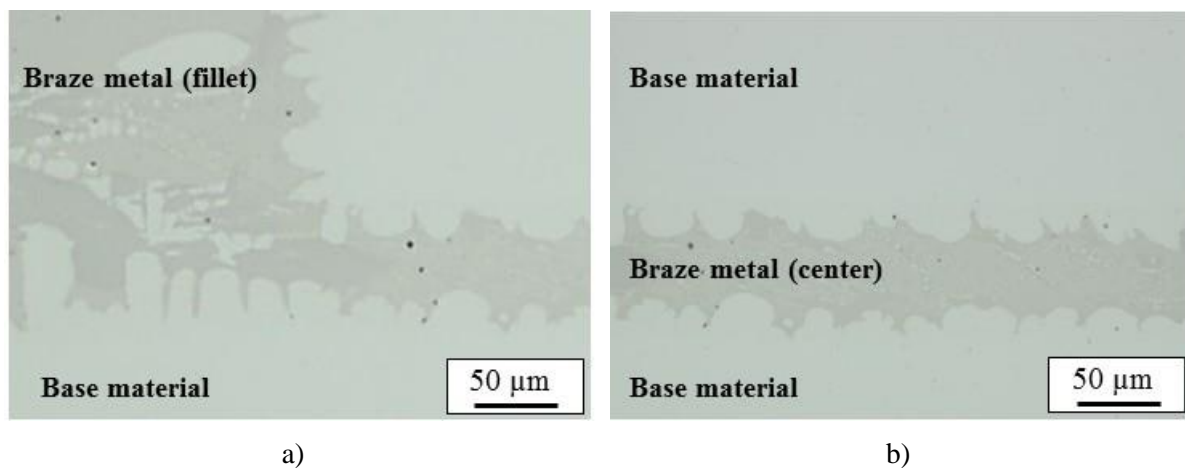


Figure 1. Light microscope image of the sample, brazed with Ni710: a) area of braze fillet; b) sample center

The brazed single lap samples, used for the analysis of the nitrogen enrichment and the corrosion measurements, were produced at temperatures of 1000 °C, 1125 °C and 1150 °C in a vacuum furnace and a continuous furnace in process gas, Table 1. The heating rate and cooling rate was adjusted at 50 K/min in both furnaces. The brazing process in the continuous furnace was carried out using different holding times of 5 min and 10 min and different process gases, 100% N₂ and 50% N₂/50% H₂. The brazing temperature was recorded as sample temperature by a trailing thermocouple attached just below the sample surface. In the vacuum furnace, a holding time of 10 min and a cooling process in an argon atmosphere were performed. The brazing temperature was measured by a thermocouple, attached in the base material below the brazed surface.

Table 1: Overview of the brazed samples

Brazing filler	Continuous furnace				Vacuum furnace
	Holding time				
	5 min		10 min		10 min
	Process gas				
	100% N ₂	50% N ₂ /50% H ₂	100% N ₂	50% N ₂ /50% H ₂	0% N ₂
NiCrP (Ni710) T _{Brazing} = 1000°C					
NiCrPSi T _{Brazing} = 1125°C					
NiCrSi (Ni650) T _{Brazing} = 1150°C					

3. Results and discussion

3.1. Analysis of the nitrogen enrichment

A quantitative determination of the nitrogen enrichment in the braze metal as well as in the base material are possible by means of CGHE. For this purpose, sample masses of about 100 mg are required. The process principle is described by Bagel [9]. Specific areas of the overlap samples are extracted by milling using a cutter with an associated cemented carbide indexable insert. The sample preparation for the analysis of the nitrogen enrichment is schematically presented in figure 2. The surface of the base material is cut off on the surface of the upper part of the sample in a depth of 100 μm . The braze metal is cut out of the braze fillet and the wetted surface without contact to the base material. The emerging material chips are used for CGHE.

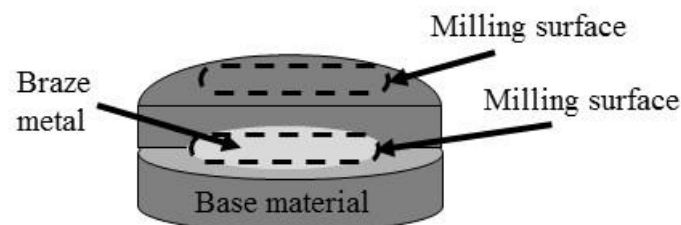


Figure 2. Scheme of sample preparation for the analysis of nitrogen enrichment

At first, the contents of N_2 in the brazing fillers and the base material were measured in the as-delivered condition. The values are 0.02 wt.% for Ni710, 0.04 wt.% for NiCrPSi and 0.05 wt.% for Ni650. The difference in the contents can be explained by the different chemical compositions of the used fillers. The N_2 content of the base material is 0.07 wt.%. After that, the N_2 contents of vacuum brazed samples were measured. The values are 0.06 to 0.07 wt.% in the base material and 0.03 to 0.06 wt.% in the braze metal. As expected, the vacuum brazing process does not influence the N_2 contents of base material and braze metal in comparison to the as-delivered condition. In case of samples that were brazed in the continuous furnace, the brazing process influences the N_2 contents of base material and braze metal significantly. In figure 3, the measured values of N_2 in the braze metal and in the base material are shown as a function of the brazing temperature resp. brazing fillers. With an increase of the brazing temperature and the use of a higher melting brazing filler, the N_2 contents in the braze metal as well as in the base material increase. This can be explained by an enhanced diffusion of nitrogen atoms into the braze metal and the base material, as it is known from nitriding processes of steels. The higher the temperature, the faster the diffusion of N_2 atoms takes place [10]. Additionally, it was found out that the process parameters holding time and N_2 content in process gas, do not have a significant influence on the N_2 contents of base material and braze metal. Hence, the scatter of the values is shown as standard deviation in the diagram. The braze metal is more intensely enriched with N_2 in comparison to the base material. The difference can be explained by the fact that liquid metals can absorb a higher amount of N_2 in comparison to solid metals, which is dissolved in the braze metal after solidification. During the brazing process, the braze metal is liquid while the base material is in the solid state.

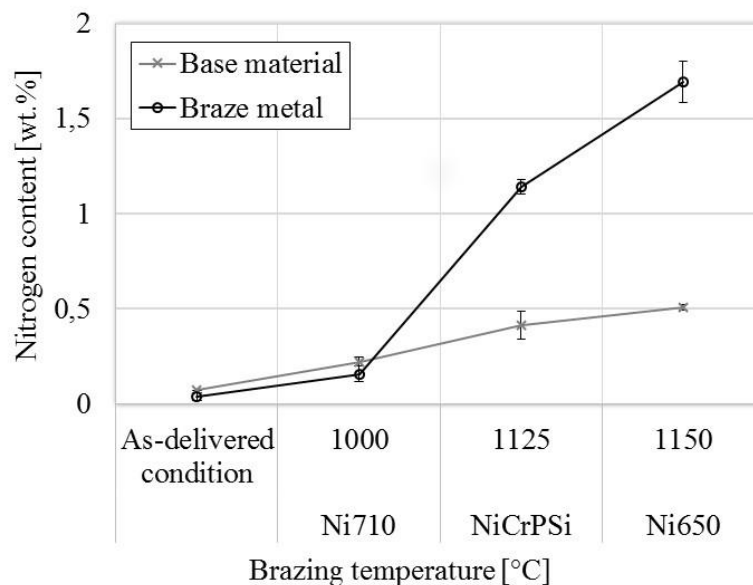


Figure 3. Nitrogen contents in the braze metal and in the base material as a function of the brazing temperature resp. brazing fillers, determined by CGHE

3.2. Corrosion measurements using a capillary microcell

The influence of the nitrogen enrichment on the corrosion behavior is analyzed using a capillary microcell. The measurement principle of capillary microcell and the measurement positions on the brazed joints are schematically presented in figure 4. A drop of electrolyte is precisely applied on the tested sample using a capillary microcell. The aggressive model condensate K 1.2 ($H_2SO_4 + HNO_3$ (pH 1.2) + 1000 mg/l NaCl) electrolyte and an Ag/AgCl electrode are used [11]. For the measurements, a capillary with a diameter of 70 μm was chosen. In this case, the different microstructure components of the brazed joints can be examined. The corrosion measurements of the base material are performed at different

positions: in the cross-section (point 1), in the cross-section near the braze fillet (point 2) on the surface (point 3) as well as in the cross-section on the braze metal (point 4), figure 4. It was determined that the corrosion potentials from point 1 do not differ for all the samples brazed in a vacuum and a continuous furnace. This can be explained by the fact that the base material is in the solid state during the brazing process and the nitrogen does not have driving forces to diffuse into the depth of the base material. Additionally, the corrosion potential of point 1 is also similar to that of point 2. Consequently, there is no influence of the process atmosphere on the corrosion behavior of the base material at these positions.

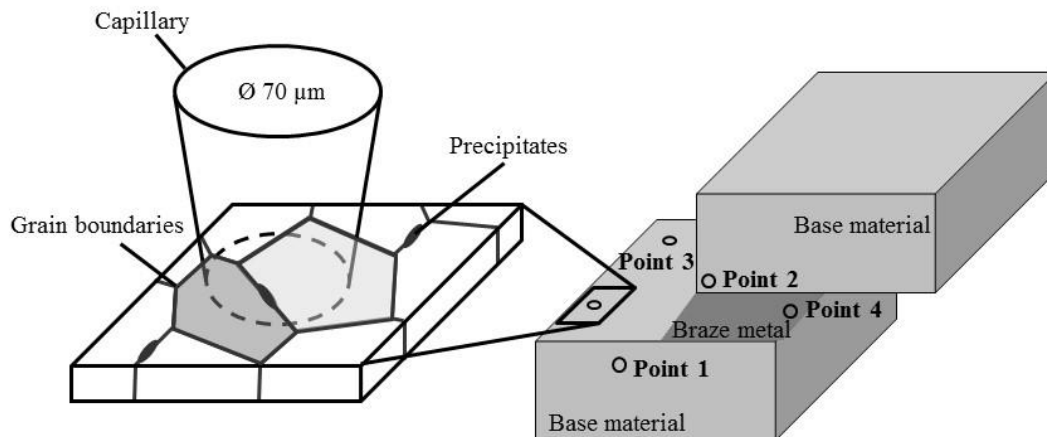


Figure 4. Principle of capillary microcell measurement and measurement positions on the samples

In figure 5, the corrosion potentials of the base material (point 3) and the braze metal (point 4) are presented as a function of the brazing temperature and the brazing fillers, respectively. It was found out that the used holding times and the N_2 contents in the process gas during continuous furnace brazing have a minor influence on the corrosion potentials of the base material and the braze metal. Hence, the scatter of the values is shown as standard deviation in the diagram. With an increase of the brazing temperature, the corrosion potentials get more negative in all cases. In comparison to the reference sample in the as-delivered condition (-300 mV), the corrosion potential of the base material is more positive for all brazed samples. During the brazing process, the oxide layer on the surface of the base material is affected. The samples that were brazed in process gas show a negative shift of the corrosion potential of -80 to -100 mV in comparison to the vacuum brazed samples dependent on the brazing temperature. That means, the base material of the samples that were brazed in process gas, becomes more ignoble than those of the vacuum brazed samples. This is caused by the enrichment of the base material with N_2 during the brazing in process gas.

The braze metals show less negative corrosion potentials than the base materials for both brazing processes. As already mentioned, liquid metals can absorb a higher amount of N_2 in comparison to solid metals. It was determined that nitrogen in the process gas causes a shift in the corrosion potentials of the braze metal. When compared to the vacuum brazed samples, the braze metals of samples, that were brazed in process gas, show a positive shift of the corrosion potential of about 10 to 30 mV dependent on the brazing temperature. It means that the braze metal of the joints is more noble than that of the vacuum brazed joints. This effect can be explained by the nitrogen enrichment, determined by means of CGHE, in the braze metal as well as in the base material.

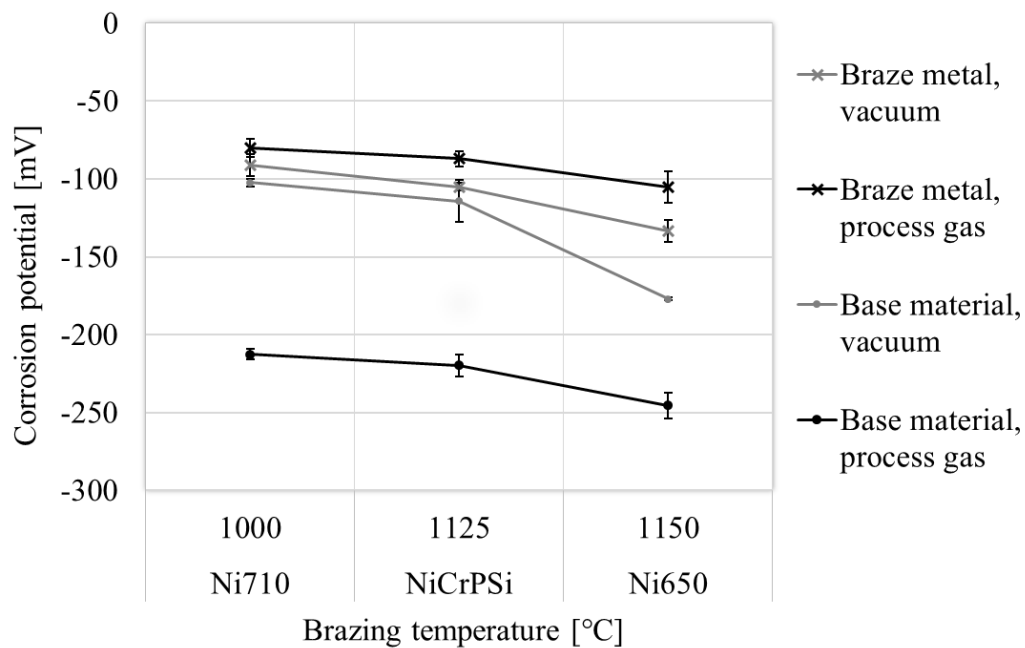


Figure 5. Corrosion potentials of the braze metal and the base material as a function of the brazing temperature resp. brazing fillers

All samples were observed using a light microscope after the capillary microcell measurements. The results of the corrosion measurements on the braze metal of the joints (point 4), brazed with Ni710 without influence of N_2 (vacuum) and with influence of N_2 (process gas), are exemplarily presented in figure 6. It can be seen that the braze metal of the joint, brazed in vacuum, is slightly more affected by the corrosion in comparison to the joint, brazed in process gas (black spots in the measurement point). This confirms the obtained results of corrosion measurements, shown in figure 5.

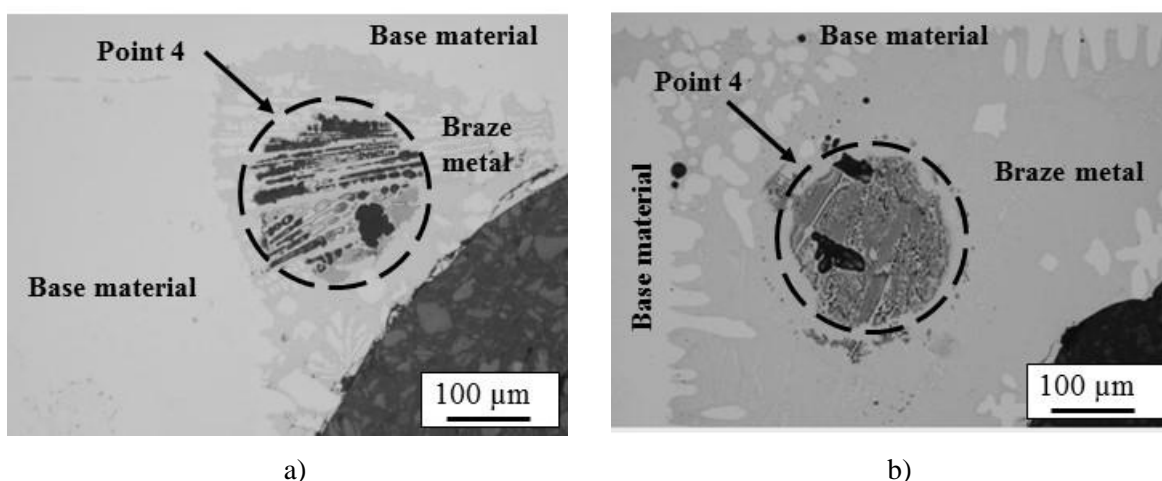


Figure 6. Corrosion measurements on the braze metal of the joints (point 4), brazed with Ni710: a) vacuum; b) process gas

4. Conclusions

The joints were produced using nickel-based brazing fillers at temperatures of 1000 °C, 1125 °C and 1150 °C in a vacuum furnace and a continuous furnace. The N₂ content in the braze metal as well as in the base material was determined by CGHE. It was found out that the different process parameters (holding time and N₂ content in the process gas) during continuous furnace brazing do not have a significant influence on the N₂ contents in the base material and the braze metal. In its turn, the samples, brazed in a continuous furnace, are more intensely enriched with nitrogen in comparison to samples in the as-delivered condition and vacuum brazed samples. With an increase of the brazing temperature and the use of a higher melting brazing filler, the N₂ content in the braze metal as well as in the base material increases for the joints that were brazed in a continuous furnace. Additionally, it was determined that the braze metal is more intensely enriched with nitrogen in comparison to the base material. The influence of the nitrogen enrichment on the corrosion behavior is analyzed using a capillary microcell. The different braze metals show less negative corrosion potentials than the base materials for both brazing processes. With an increase of the brazing temperature, the corrosion potentials are more negative in all cases. Additionally, it was determined that nitrogen in the process gas causes a shift in the corrosion potentials of the braze metal and the base material. In case of the braze metal, the nitrogen influences the corrosion potential of the brazed joint positively. In contrast to that, the nitrogen has a negative influence on the corrosion potential of the base material. It was also supposed, that nitrogen can influence the fatigue behavior of stainless steel joints, brazed with nickel-based fillers [8]. In further investigations, the fatigue behavior of brazed stainless steel joints will be observed.

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